

Effective Hamiltonians for state selection in Heisenberg antiferromagnets

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(Dated: September 28, 2009)

In frustrated antiferromagnets with isotropic exchange interactions, there is typically a manifold of degenerate classical ground states. This degeneracy is broken by the (free) energy of quantum or thermal fluctuations, or the uniform effects of bond disorder. We derive effective Hamiltonians to express each kind of selection effect, in both exact forms and convenient approximate forms. It is argued that biquadratic terms, representing the collinear-selecting effects of quantum fluctuations, should be included in classical simulations of large- S frustrated magnets at low temperatures.

PACS numbers: 75.10.Hk, 75.10.Jm, 75.50.Lk, 75.25.+z

I. INTRODUCTION

This paper concerns antiferromagnets with isotropic exchange couplings, i.e. the Hamiltonian has form

$$\mathcal{H}_{\text{ex}} = -\frac{1}{2} \sum_{i \neq j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j. \quad (1.1)$$

(Such sums will always run to N , the number of spins.) When the interactions in (1.1) are frustrated, the classical ground states often exhibit continuous *nontrivial* degeneracies — beyond those induced by the global spin symmetry. In a *highly* frustrated antiferromagnet¹, the number of such degrees of freedom is extensive; in other cases, such as face-centered cubic (fcc) antiferromagnets, it is a finite-dimensional manifold. In either case, such degeneracies are lifted by thermal fluctuations, quantum fluctuations, or quenched fluctuations (due to dilution). The selection of a ground state due to fluctuations was called² (by a slight abuse of terminology) *ordering by disorder*.³ The purpose of this paper is to provide effective Hamiltonians, in convenient form, which represent the degeneracy-breaking selection (free) energy.

A ground state selection calculation for a continuous spin system was performed first by Shender, who showed that in the two-sublattice garnet $\text{Mn}_3\text{Cr}_2\text{Ge}_3\text{O}_{12}$ quantum fluctuations favor a collinear spin configuration.⁴ The selection causes an effective “anisotropy” of one sublattice relative to the other, which opens a gap in some soft spin wave modes observable in neutron scattering.^{5,6} Others have calculated a similar effect for the type I FCC antiferromagnet $\gamma\text{-Mn}_p\text{Fe}_{1-p}$ ^{7,8,9}. Rastelli and co-workers investigated thermal and quantum fluctuations in the frustrated rhombohedral lattice (describing $\beta\text{-O}_2$), finding again that quantum fluctuations select collinear ground states¹⁰. The collinearity bias was decisive between different possible fcc orderings in Cu nuclear spins^{11,12}. Quantum fluctuations were also found to decide the ground state in $\text{Sr}_2\text{Cu}_3\text{O}_4\text{Cl}_2$ ¹⁴.

Whereas thermal or quantum fluctuations select *collinear* states^{4,13} quenched fluctuations due to dilution select *non-collinear* states^{2,13}, in cases where the ground state manifold is finite dimensional. (In *highly* frustrated magnets, meaning

the degrees of freedom are extensive, the many zero-energy excitations “screen” defects and dilution does not necessarily favor a global noncollinear state^{15,16}.) The competing selection effects can give a rich phase diagram as a function of temperature and dilution, as simulated in the J_1 - J_2 square lattice antiferromagnet^{13,17,18,20}. In particular, making use of the effective Hamiltonians presented in this paper, we studied the fcc type III antiferromagnet with dilution and Dzyaloshinskii-Moriya anisotropic exchange¹⁹; this represents the antiferromagnetic dilute magnetic semiconductor $\text{Cd}_{1-p}\text{Mn}_p\text{Te}$ for $x \rightarrow 1$, a material realized using molecular-beam epitaxy^{21,22}.

For all three kinds of selection – thermal, quantum, and dilution – the selection is conveniently expressed by adding biquadratic exchange terms to the Hamiltonian,

$$\mathcal{H}_{\text{biq}} = -\frac{1}{2} \sum_{ij} K_{ij} (\mathbf{S}_i \cdot \mathbf{S}_j)^2. \quad (1.2)$$

Such a form is quite familiar for selection by quantum fluctuations in the “independent sublattices” case, i.e. the antiferromagnet consists of two (pr more) sublattices with a strong, unfrustrated intra-lattice interaction J_1 , and a weak, frustrating inter-lattice interaction J_2 ^{4,5,13,23}. Eq. (1.2) follows directly from perturbation in J_1/J_2 , with inter-sublattice $K_{ij} = O(J_1^2/J_2)$. However, there are many other cases in which the degeneracy freedom requires correlated rotations in all the sublattices. This paper lays out the framework in which (1.2) can be justified (approximately) in that broader class of frustrated systems.

In Sec. II we present a microscopic calculation of the free energy in the presence of quenched disorder and thermal fluctuations, performed to lowest nontrivial order in spin deviations. The combined selection effects are extracted in a new way by performing a constrained integration over the fluctuations in reciprocal space. Then, in Sec. II B we express the results in the phenomenological form of an effective biquadratic exchange term. In Sec. III, quantum fluctuations are shown to give a similar form, using an approximation of the spin-wave approximation. Appendices A and B give, respectively, an alternate path to the dilution effective Hamiltonian, and a

calculation of magnetoelastic effects (which reduce to a similar quartic effective Hamiltonian, and thus give selection effects similar to those of thermal or quantum fluctuations). The Discussion (Sec. IV) proposes applications for the effective Hamiltonian in working out phase diagrams in simulations of magnetic systems.

II. THERMAL FLUCTUATIONS AND DILUTION

In this section we show that thermal fluctuations favor collinear states while dilution favors the least collinear states. This competition is a general feature of all uniformly frustrated vector spin systems studied so far and has a simple explanation^{2,13}. It is familiar that spins in a vector antiferromagnet will orient transverse to an applied magnetic field, because they can thereby gain energy by relaxing towards it. The *effective* local fields generated by thermal fluctuations are transverse to the fluctuating spins, and the free energy will be lower when other spins are transverse to these effective fields. The coupling, and the entropy, is therefore maximized when all spins are *collinear*⁴.

By contrast, dilution (the removal of spins) generates effective fields parallel to the removed spins (or other spins of the same sublattice). In this case the energy is minimized for the *least* collinear states, because most spins are again transverse to the effective field acting on them. The above qualitative arguments will be confirmed by perturbative spin-mode calculations.

In the rest of this section, we first set up the artificial form of dilution; then, representing a delta function by auxiliary variables, we sidestep the awkwardnesses expanding about a general nonperiodic, noncollinear classical ground state (Subsec. II A). This result can be put in the form of a biquadratic effective Hamiltonian (Sec. II B).

A. Formal Derivation of Selection Free Energy

For this section, the spins in (1.1) are taken to be classical unit vectors with n components. We compute the free energy by assuming the fluctuations about the ground state are small,

$$\mathbf{S}_i = \mathbf{S}^{(0)}_i + \boldsymbol{\sigma}_i, \quad \mathbf{S}^{(0)}_i \cdot \boldsymbol{\sigma}_i = 0, \quad (2.1)$$

and $|\boldsymbol{\sigma}| \ll 1$. Further, we will consider “modulation” disorder where the exchange between sites i and j is increased or decreased by the independent random variables ϵ_i . The actual couplings are taken to be

$$J_{ij}^{\text{real}} = J_{ij}(1 - \epsilon_i)(1 - \epsilon_j), \quad (2.2)$$

with $\langle \epsilon_i \rangle = 0$. This approximation²⁴ lets us control the size of the deviations $\boldsymbol{\sigma}_i$ by taking the variance of the random modulation to be a small parameter: $\langle \epsilon_i^2 \rangle \equiv \langle \epsilon^2 \rangle \ll 1$. We will take $J'_{ij} = J_{ij}^{\text{pure}}$ for modulation disorder, where J_{ij}^{pure} is the energy of a bond in the pure system.

True site dilution means $J_{ij}^{\text{real}} = J_{ij}^{\text{pure}} \eta_i \eta_j$, where the random variable η_i is 1 (site occupied) with probability p and zero

with probability zero. (See Appendix A.) This takes the form of Eq. (2.2), with $\langle \epsilon_i \rangle = 0$, if we take $\epsilon_i \equiv 1 - \eta_i/p$. This then forces $J_{ij} = p^2 J_{ij}^{\text{pure}}$.

For the “independent lattices” case e.g. the type II bcc^{4,5}, the type II FCC ordering, the frustrated square lattice model¹³, or a body-centered tetragonal antiferromagnet²³, the ratio J_1/J_2 can be a small parameter for achieving this same control in the limit of large $|J_2|$, because the noncollinear part of the effective field of a missing spin becomes small compared to the collinear part. In Appendix A it is shown that the model of (2.2) and true dilution are equivalent to lowest order in the spin fluctuations. Monte Carlo results for true dilution are consistent with the results of this theory for $p \lesssim 1$.^{19,20}

The ground state condition is that $\mathbf{S}_i^{(0)} = \mathbf{h}_i^{(0)}/|\mathbf{h}_i^{(0)}|$ for all i , i.e. every spin is aligned with its “local field”

$$\mathbf{h}_i^{(0)} \equiv \sum_j J_{i,j} \mathbf{S}_j^{(0)}. \quad (2.3)$$

We assume $|\mathbf{h}_i^{(0)}| \equiv h_0$, the same at every site (subsequent manipulations depend on this.) The assumption is valid on most cases that the sites are symmetry-equivalent, even in highly frustrated systems (e.g. pyrochlore lattice) where a generic ground state is not at all periodic. Substituting (2.3) in (1.1) shows $E_0 = h_0/2$, so h_0 must be the same in every ground state, too.

Expanding in small deviations, the Hamiltonian (1.1) becomes a quadratic form

$$\begin{aligned} \mathcal{H}_{\text{quad}} - NE_0 &= \sum_i \mathbf{h}_i \cdot \mathbf{S}^{(0)}_i + \sum_i \mathbf{h}_i \cdot \boldsymbol{\sigma}_i \\ &\quad + \frac{1}{2} \sum_{ij} A(i,j) \boldsymbol{\sigma}_i \cdot \boldsymbol{\sigma}_j + \mathcal{O}(\epsilon^3) \end{aligned} \quad (2.4)$$

Here E_0 is the ground state energy per spin of the pure system, and

$$\mathbf{h}_i \equiv \sum_j J_{i,j} \epsilon_j \mathbf{S}_j^{(0)}. \quad (2.5)$$

Also,

$$A_{i,j} \equiv -J_{i,j} + h_0 \delta_{ij}. \quad (2.6)$$

The first term on the right hand side of (2.4) is independent of $\boldsymbol{\sigma}_i$ and vanishes when the configurational averages are taken. We ignore the last term since it is higher order in ϵ .

1. Evaluation via auxiliary representation of constraints

We now have a Hamiltonian which is purely quadratic and apparently trivial. However, as always, each spin really has only $n - 1$ degrees of freedom since its length is fixed. When $n > 2$, there is an arbitrariness in the choice of basis vectors for the local transverse subspace, a gauge freedom. It is cumbersome to fix this gauge by a choice of local frames²⁶. Instead, following Ref. 2 we shall implement the constraints

so as to avoid introducing an explicit local frame for each spin, using integral identities to maintain a manifestly rotation-invariant (gauge-invariant) form.

For convenience, a matrix notation will be used where the matrix indices specify both position (i) and vector component in spin space (μ). The unit length constraint becomes

$$\mathbf{P} \cdot \boldsymbol{\sigma} = 0. \quad (2.7)$$

Here \mathbf{P} is the nonsquare ($N \times Nn$) matrix whose components are

$$P_{i,i'\mu'} = \delta_{i,i'} S^{(0)}_{i'\mu'}. \quad (2.8)$$

Since $\mathbf{S}_i^{(0)}$ is a unit vector,

$$\mathbf{P}\mathbf{P}^T = \mathbf{I}_{N \times N}, \quad (2.9)$$

where \mathbf{I} is the identity matrix, and we (sometimes) add a subscript to clarify a matrix's dimension. (However, notice $\mathbf{P}^T\mathbf{P} \neq \mathbf{I}_{Nn \times Nn}$.) The definition of $A_{i,j}$ [Eq. (2.6)] becomes

$$\mathbf{A} = -\mathbf{J} + h_0\mathbf{I}. \quad (2.10)$$

In (2.10), the matrices \mathbf{A} and \mathbf{J} are $N \times N$, but from here till the end of the section they are extended to be $Nn \times Nn$ matrices (by taking the direct product with $\mathbf{I}_{n \times n}$, acting on the spin indices). Also, \mathbf{h} [from (2.5)] becomes an Nn -component vector in this notation.

Our goal, the partition function for Hamiltonian (2.4), is

$$Z = \int \left[\prod_{i\mu} d\boldsymbol{\sigma}_{i\mu} \right] \left[\prod_j \delta(\mathbf{P} \cdot \boldsymbol{\sigma}) \right] \exp \left(-\frac{1}{2} \beta \boldsymbol{\sigma}^T \mathbf{A} \boldsymbol{\sigma} + \beta \mathbf{h}^T \boldsymbol{\sigma} \right). \quad (2.11)$$

By representing the delta function of the constraints in terms of a functional integral of $\exp(it\mathbf{P}\boldsymbol{\sigma})$ over auxiliary variables $\{t_i\}$ and completing the square in the resulting exponential, the $d\boldsymbol{\sigma}_{i\mu}$ integral can be done², yielding

$$Z = Z_1 \int \left[\prod_i \frac{dt_i}{2\pi} \right] \exp \left(-\frac{1}{2} (\mathbf{h}^T + i\beta^{-1} \mathbf{t}^T \cdot \mathbf{P}) \mathbf{A}^{-1} (\mathbf{h} + i\beta^{-1} \mathbf{P}^T \cdot \mathbf{t}) \right). \quad (2.12)$$

Here

$$\begin{aligned} Z_1 &\equiv \int \left[\prod_{i\mu} d\boldsymbol{\sigma}_{i\mu} \right] \exp \left(-\frac{1}{2} \beta \boldsymbol{\sigma}^T \mathbf{A} \boldsymbol{\sigma} \right) \\ &= \left(\frac{2\pi}{\beta} \right)^{\frac{Nn}{2}} (\det \mathbf{A})^{-\frac{1}{2}}. \end{aligned} \quad (2.13)$$

To make further progress, let us define the ($N \times N$) matrix of the quadratic coefficients in (2.12):

$$\mathbf{B} \equiv \mathbf{P} \mathbf{A}^{-1} \mathbf{P}^T, \quad (2.14)$$

All our results will be expressed in terms of \mathbf{B} . Since \mathbf{B} is nonsingular, we can evaluate (2.12) using a second completion of squares²⁷.

Thus,

$$Z = Z_1 Z_2 e^{-\beta \Delta F}, \quad (2.15)$$

where

$$Z_2 \equiv \int \left[\prod_i \frac{dt_i}{2\pi} \right] e^{-\frac{1}{2} \beta^{-1} \mathbf{t}^T \mathbf{t}} = [2\pi\beta]^{\frac{N}{2}} (\det \mathbf{B})^{-\frac{1}{2}}, \quad (2.16)$$

and

$$\Delta F \equiv -\frac{1}{2} \mathbf{h}^T \left(\mathbf{A}^{-1} - \mathbf{A}^{-1} \mathbf{P}^T \mathbf{B}^{-1} \mathbf{P} \mathbf{A}^{-1} \right) \mathbf{h}. \quad (2.17)$$

2. Free energy result and disorder average

Thus the exact free energy is

$$\begin{aligned} F &= -\beta^{-1} \left[N \left(1 + \frac{n}{2} \right) \ln(2\pi) + N \left(1 - \frac{n}{2} \right) \ln \beta - \frac{1}{2} \ln(\det \mathbf{A}) \right] \\ &\quad + \beta^{-1} \frac{1}{2} \ln(\det \mathbf{B}) + \Delta F - \mathbf{h}^T \cdot \mathbf{S}^{(0)} \\ &\equiv F_0 + F_T + F_{\text{dil}} + F_{\text{REF}} \equiv F_0 + F_{\text{sel}}, \end{aligned} \quad (2.18)$$

where we have reintroduced the linear term in \mathbf{h} from (2.4). In this equation, the term in brackets (F_0) is independent of the ground state, hence irrelevant for state selection (though possibly important in comparing to the free energy of competing orders). The remaining three terms constitute the *selection free energy*: respectively, thermal selection, dilution selection term, and finally F_{REF} linear in the effective fields caused by dilution. The disorder average of F_{REF} is clearly zero, but such terms give “random exchange fields”, so called as they (may) act like a random field on the discrete order parameter remaining after selection^{2,18,19,28}.

Next we average F_{sel} over disorder. Recall from (2.5) that $\mathbf{h} = \mathbf{J}\mathbf{P}^T\boldsymbol{\epsilon}$ and $\langle \epsilon_i \epsilon_j \rangle = \delta_{i,j} \langle \epsilon^2 \rangle$ allows us to average $\Delta F \equiv F_{\text{dil}}$ [given by (2.17)]:

$$\langle F_{\text{dil}} \rangle = -\frac{1}{2} \langle \epsilon^2 \rangle \text{Tr} \left[\mathbf{P} \mathbf{J} (\mathbf{A}^{-1} - \mathbf{A}^{-1} \mathbf{P}^T \mathbf{B}^{-1} \mathbf{P} \mathbf{A}^{-1}) \mathbf{J} \mathbf{P}^T \right] \quad (2.19)$$

Substituting $\mathbf{J} \rightarrow h_0\mathbf{I} - \mathbf{A}$ from (2.10), Eq. (2.19) expands into zero, first, and second order terms in h_0 . By repeated use of (2.9) and (2.14), the contributions of the two terms in parentheses inside (2.19) are seen to cancel in both the $O(h_0)$ and $O(h_0^2)$ parts of the expansion. The result is

$$\langle F_{\text{dil}} \rangle = -\frac{1}{2} \langle \epsilon^2 \rangle \text{Tr} (\mathbf{P} \mathbf{A} \mathbf{P}^T - \mathbf{B}^{-1}) \quad (2.20)$$

Now $\text{Tr}(\mathbf{P} \mathbf{A} \mathbf{P}^T) = \text{Tr}(\mathbf{A}_{N \times N}) = Nh_0$, which is the same for all ground states. Gathering terms, the averaged selection free energy is

$$\langle F_{\text{sel}} \rangle = \frac{1}{2} k_B T \text{Tr}(\ln \mathbf{B}) + \frac{1}{2} \langle \epsilon^2 \rangle \text{Tr}(\mathbf{B}^{-1}) - \frac{1}{2} \langle \epsilon^2 \rangle Nh_0, \quad (2.21)$$

where we have used $\ln(\det \mathbf{B}) = \text{Tr}(\ln \mathbf{B})$.

It can be shown that (2.20) vanishes for collinear states and is *negative* semidefinite (see Appendix A). Therefore dilution must favor noncollinear states.

B. Effective Hamiltonian for Selection

In this section we re-express the classical selection (free) energy (2.21) in the form of an effective Hamiltonian. In this form, it is easy to join the selection terms with other perturbations that also tend to select states, such as anisotropies or magnetoelastic couplings. The selection term takes the biquadratic form (1.2). for all exchange-coupled frustrated vector magnets.

In the J_1 - J_2 antiferromagnets on the square lattice $[(\pi, 0)$ order], the fcc lattice (type II order) or the bcc lattice (bcc type II order), the ground states consist of sublattices which can rotate independently of each other (provided order-by-disorder is neglected!). These sublattices are connected only by J_1 interactions, so J_1/J_2 can be used as a small parameter. Indeed, the lowest-order term in the J_1/J_2 expansion does have the biquadratic form (1.2) for the J_1 - J_2 XY model on the square lattice¹³ or for quantum fluctuations in the large- S Heisenberg model on the bcc⁴. However, for many other cases (e.g. fcc type I or type III), the degeneracies entail correlated changes in different sublattices, so there is no natural small parameter.

We deploy a different trick, which has no guaranteed small parameter. It is based on the central role played by the matrix \mathbf{B} in the previous subsection. Recall (2.21) gave the selection free energy in terms of $\ln \det \mathbf{B}$ and $\text{Tr} \mathbf{B}^{-1}$. The matrix \mathbf{B} was defined in real space by (2.14) as

$$\mathbf{B}_{ij} = \mathbf{S}_i \cdot \mathbf{S}_j G_{ij} \quad (2.22)$$

where

$$G_{ij} \equiv (\mathbf{A}^{-1})_{ij}. \quad (2.23)$$

is a Green's function. (For this section, we drop the superscript in $\mathbf{S}_i^{(0)}$; it is understood that \mathbf{S}_i is a mean direction.) Although G_{ij} has the translational invariance of the lattice, it is *not* simply a function of $\mathbf{r}_i - \mathbf{r}_j$ if the sites do not form a non-Bravais lattice (e.g. honeycomb, garnet, or pyrochlore lattices). Since the \mathbf{A} matrix is a discrete approximation of the Laplacian, G_{ij} is likely to behave at long distances as $1/r_{ij}$ (in $d = 3$) or as $\ln r_{ij}$ (in $d = 2$).

Now for the trick: let $\bar{\mathbf{B}}$ be the average of \mathbf{B} over the whole ground state ensemble,

$$\bar{\mathbf{B}}_{ij} = \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle_s G_{ij}, \quad (2.24)$$

where the angle brackets refer to an unweighted average over all ground states.²⁹ (Notice $\bar{\mathbf{B}}$ has the full symmetry of the lattice, higher symmetry than \mathbf{B} has.) We shall formally consider

$$\delta \mathbf{B} \equiv \mathbf{B} - \bar{\mathbf{B}} \quad (2.25)$$

to be our small parameter. Thus

$$\delta \mathbf{B}_{ij} = G_{ij} (\mathbf{S}_i \cdot \mathbf{S}_j - \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle_s) \quad (2.26)$$

Then from (2.21) by expanding the logarithm of \mathbf{B} (for thermal selection) or its inverse (for dilution selection) in powers of $\delta \mathbf{B}$, we arrive at

$$\langle F_{\text{sel}} \rangle \approx [f_{\text{sel}}^{(0)} + f_{\text{sel}}^{(1)} + f_{\text{sel}}^{(2)}], \quad (2.27)$$

where $f_{\text{sel}}^{(m)}$ is the $O((\delta \mathbf{B})^m)$ term. In (2.27),

$$f_{\text{sel}}^{(0)} = \frac{1}{2} k_B T \ln(\det \bar{\mathbf{B}}) + \frac{1}{2} \langle \epsilon^2 \rangle \text{Tr}(\bar{\mathbf{B}}^{-1}), \quad (2.28)$$

$$f_{\text{sel}}^{(1)} = \frac{1}{2} \sum_{i,j} J_{ij}^{\text{eff}} \mathbf{S}_i \cdot \mathbf{S}_j, \quad (2.29)$$

where

$$J_{ij}^{\text{eff}} \equiv 2k_B T \sum_{i,j} (\bar{\mathbf{B}}^{-1})_{ij} G_{ji} - 2 \langle \epsilon^2 \rangle \sum_{i,j} (\bar{\mathbf{B}}^{-2})_{ij} G_{ji}; \quad (2.30)$$

and

$$f^{(2)} = -\frac{1}{4} \sum_{i,j,k,l} K_{ij,kl} (\mathbf{S}_j \cdot \mathbf{S}_k) (\mathbf{S}_l \cdot \mathbf{S}_i), \quad (2.31)$$

with

$$K_{jk,li} \equiv G_{jk} G_{li} \left[k_B T (\bar{\mathbf{B}}^{-1})_{ij} (\bar{\mathbf{B}}^{-1})_{kl} + \langle \epsilon^2 \rangle (\bar{\mathbf{B}}^{-2})_{ij} (\bar{\mathbf{B}}^{-1})_{kl} \right]_{\text{symm}} \quad (2.32)$$

Here “symm” means the expressions are to be symmetrized over all distinct ways of pairing indices, such that each pair has one from jk and one from li (two or four ways, respectively, in the two terms). Each term includes contributions from both F_T and F_{dil} .

Clearly $f^{(0)}$ does not cause selection, since it produces only constants dependent on T and $\langle \epsilon^2 \rangle$. As for the $f^{(1)}$ term of (2.32), it takes the form of a renormalization of the ordinary exchange couplings $J_{ij} \rightarrow J_{ij} + \delta J_{ij}$, where

$$\delta J_{ij} \equiv 2k_B T (\bar{\mathbf{B}}^{-1})_{ij} G_{ji} - 2 \langle \epsilon^2 \rangle \sum_{i,j} (\bar{\mathbf{B}}^{-2})_{ij} G_{ji}. \quad (2.33)$$

(Here δJ_{ij} has the full lattice symmetry, since $\bar{\mathbf{B}}$ and G_{ij} do.) Within the ground state manifold, $f^{(1)}$ is normally constant (assuming the degeneracy is generic by symmetry, and not due to a particular ratio of the couplings). Nevertheless, the renormalization will shift the phase boundary between the kind of order in question and a competing spin order.

When can we simplify $f^{(2)}$? Commonly, and certainly when the sites form a Bravais lattice^{30,32} one can write any classical ground state as a linear combination of the (degenerate) optimal eigenvectors of the J_{ij} matrix, the so-called Luttinger-Tisza construction³¹. The (vector valued) coefficients play the role of order parameter components $\{\mathbf{N}_\alpha\}$. Obviously, $f^{(2)}$ will be quartic in $\{\mathbf{N}_\alpha\}$. If group theory tells us there are m independent quartic combinations – $m = 2$ for the type III fcc antiferromagnet¹⁹ – then the parameter space of possible $f^{(2)}$ functions is only m dimensional. We could exactly reproduce these functions using (1.2) out to the m -th nearest neighbor.

C. Real-space perturbation approach

There is an alternative, cruder path to the biquadratic form, in the case of classical thermal fluctuations²⁵. It is included

here because it is fully analogous to the approach we use for quantum selection in Sec. III.

The idea in this approach is to treat the site-diagonal part of (2.4) as the zero-order part, and to pretend the inter-site terms are a small perturbation \mathcal{H}' . (In fact the site-diagonal and inter-site coefficients are manifestly the same order in the $J_{i,j}$'s. However, as elaborated in Sec. III B, we may consider $1/z$ to be a sort of small parameter, where z is the coordination number.)

We continue to assume that the local field h_0 is the same on every site. Thus our zero-order Hamiltonian is quite trivial and tractable, and the perturbation free energy is derived from the cumulant expansion to second order:

$$\mathcal{H}_{\text{eff}} = -\langle \mathcal{H}'^2 \rangle_0 / 2T, \quad (2.34)$$

where $\langle \dots \rangle_0$ means the expectation in the ensemble with just h_0 . (I omit the terms in $\langle \mathcal{H}' \rangle_0$, since $\langle \mathcal{H}' \rangle_0 = 0$.)

By taking expectations in this trivial ensemble, one sidesteps most technical annoyances due to the different orientations of spins, which necessitated the auxiliary integration in (2.12). We simply have

$$\langle \sigma_{i\mu} \sigma_{i\nu} \rangle_0 = \left(\delta_{\mu\nu} - n_{i\mu} n_{i\nu} \right) \frac{k_B T}{h_0} \quad (2.35)$$

where $\hat{\mathbf{n}}_i \equiv \mathbf{S}_i$. (This notation for the unit spins is consistent with Sec. III.) Then

$$\langle \mathcal{H}'^2 \rangle_0 = \sum_{ij} \left\langle (J_{ij} \boldsymbol{\sigma}_i \cdot \boldsymbol{\sigma}_j)^2 \right\rangle_0 \quad (2.36)$$

Terms mixing two different pairs vanish since $\langle \boldsymbol{\sigma}_i \rangle_0 = 0$. In (2.36),

$$\langle (\boldsymbol{\sigma}_i \cdot \boldsymbol{\sigma}_j)^2 \rangle_0 = \sum_{\mu\nu} \langle \sigma_{i\mu} \sigma_{j\mu} \sigma_{i\nu} \sigma_{j\nu} \rangle_0 \quad (2.37)$$

$$= - \sum_{\mu\nu} (\delta_{\mu\nu} - n_{i\mu} n_{i\nu}) \quad (2.38)$$

$$\times (\delta_{\mu\nu} - n_{j\mu} n_{j\nu}) \left(\frac{k_B T}{h_0} \right)^2 \\ = \left[1 + (\hat{\mathbf{n}}_i \cdot \hat{\mathbf{n}}_j)^2 \right] \left(\frac{k_B T}{h_0} \right)^2. \quad (2.39)$$

Putting it all together, we get the form (1.2) with

$$K_{i,j} = k_B T \frac{J_{i,j}^2}{h_0^2} \quad (2.40)$$

That is exactly what we would get from (2.32) if we took $A_{ij} = h_0 \delta_{ij}$ in place of (2.10), which would be consistent with our pretence that \mathbf{J} is small compared to h_0 .

III. HARMONIC QUANTUM FLUCTUATIONS

A similar effective Hamiltonian emerges from an approximate treatment of the selection due to quantum spin fluctuations within the spin-wave approximation. The basic idea of

the method was used by Long⁸ for calculating quantum selection in type I FCC antiferromagnets. We reformulate this approach to be explicitly independent of the “gauge” arbitrariness in choosing local frames (Sec. III B), and show that quantum fluctuations always favor collinear states.

A. Set-up for harmonic Hamiltonian

We start from a classical ground state spin configuration, defined by a set of classical directions $\{\hat{\mathbf{n}}_i\}$, and set up the Holstein-Primakoff representation in the standard fashion (for noncollinear spins²⁶). In contrast with Sec. II, from here on \mathbf{S} denotes the spin operator and is not normalized to unit length. A local orthonormal triad $(\hat{\mathbf{x}}_i, \hat{\mathbf{y}}_i, \hat{\mathbf{z}}_i)$ such that $\hat{\mathbf{z}}_i \equiv \hat{\mathbf{n}}_i$, and we quantize along the $\hat{\mathbf{z}}_i$ axis; we let a bar distinguish spins written in this local basis. Holstein-Primakoff bosons are introduced as usual:

$$\bar{S}_{iz} = S - a_i^\dagger a_i, \quad (3.1a)$$

$$\bar{S}_{i-} = a_i^\dagger \sqrt{2S - a_i^\dagger a_i} \quad (3.1b)$$

where $\bar{S}_{i+} = \bar{S}_{i-}^\dagger$. (We restored the explicit powers of S that were omitted in the classical discussion of Sec. II.) Of the Taylor series for the square roots, giving the semiclassical expansion in $1/S$, we just need the lowest order approximation, $\bar{S}_{i-} \approx \sqrt{2S} a_i^\dagger$. That means

$$\mathbf{S}_i \approx \bar{S}_{iz} \hat{\mathbf{z}} + \frac{\sqrt{S}}{2} (\mathbf{e}_+ a_i^\dagger + \mathbf{e}_- a_i) \quad (3.2)$$

Here $\mathbf{e}_\pm \equiv (\hat{\mathbf{x}} \pm i\hat{\mathbf{y}})/\sqrt{2}$. Next (3.2) must be substituted into the spin Hamiltonian (1.1). The zeroeth order term (in $\{a_i^\dagger\}$ and $\{a_i\}$) is the classical ground state energy, while the first order term vanishes since the ground state is classically stable (each $\hat{\mathbf{n}}_i$ is lined up with the local field \mathbf{h}_i). So we only treat the second order, i. e. harmonic terms. The resulting quadratic Hamiltonian is a quantum analog of (2.4):

$$H_{\text{harm}} = \text{const} - \sum_i h_i (S - a_i^\dagger a_i) \\ + \frac{1}{2} \sum_{ij} J_{ij} (\mathbf{e}_+ a_i^\dagger + \mathbf{e}_- a_i) (\mathbf{e}_+ a_j^\dagger + \mathbf{e}_- a_j) \quad (3.3)$$

The usual course is to (Bogoliubov) diagonalize (3.3), giving the harmonic spin wave modes and frequencies $\{\omega_m\}$. Then the harmonic zero-point energy is

$$E_{\text{harm}}(\{\hat{\mathbf{n}}_i\}) = \sum_m \frac{1}{2} \hbar \omega_m. \quad (3.4)$$

Since the spin-wave spectrum is usually different for symmetry- unrelated states, (3.4) typically breaks the degeneracy with the energy scale $O(JS)$ (down by $1/S$ compared to the total classical energy.) As in the previous section, we desire simple explicit expressions for the dependence on $\hat{\mathbf{n}}_i$ that is implicit in (3.4), i.e., an effective Hamiltonian.

To implement this for a frustrated or highly frustrated antiferromagnet requires

- (i) The assumption – not always valid – of a periodic state; in any case, the magnetic unit cell is typically large leading to large matrices;
- (ii) The choice of an explicit frame for each site, normal to its spin, as the basis for possible spin deviations, with its gauge arbitrariness²⁶;
- (iii) the calculation should be repeated for every one of its (*continuum* of) inequivalent ground states.

As in the classical selection calculation, all this makes the calculation cumbersome and sometimes impossible.

B. Real-space perturbation approach

To get an approximate answer of simple form, we shall decline to diagonalize the Hamiltonian, and instead treat the inter-spin terms in (3.3) as if they were small perturbations: that is, \mathcal{H}_0 is defined to be the first term, and \mathcal{H}' is the second term. (This was pointed out by Long⁸.)

The ground state $|0\rangle$ of \mathcal{H}_0 is unique and obviously $\bar{S}_{iz} = S$ for all sites; the first nontrivial term must come from second-order perturbation theory. The excited-states in $\mathcal{H}'|0\rangle$ have two spin flips on coupled sites (i, j) , with an excitation cost $S(h_i + h_j)$, as created by the term with two boson creations. (In most frustrated systems, $h_i = h_0$ the same on all sites, allowing for simplifications.) Thus, in second order perturbation theory, we get the correction⁸

$$\delta E = -\frac{S^2}{2} \sum_{i,j} \frac{J_{ij}^2}{h_i + h_j} |\mathbf{e}_{i+} \cdot \mathbf{e}_{j+}|^2. \quad (3.5)$$

Now we take advantage of the fact that $\{\hat{\mathbf{x}}_i, \hat{\mathbf{y}}_i, \hat{\mathbf{z}}_i\}$ are rows of a (proper) orthogonal matrix:

$$x_{i\lambda}x_{i\mu} + y_{i\lambda}y_{i\mu} + z_{i\lambda}z_{i\mu} = \delta_{\lambda\mu}; \quad (3.6a)$$

$$x_{i\lambda}y_{i\mu} - y_{i\lambda}x_{i\mu} = \epsilon_{\lambda\mu\nu}z_{i\nu} \quad (3.6b)$$

Hence, assuming the summation convention,

$$\begin{aligned} |\mathbf{e}_+ \cdot \mathbf{e}'_+|^2 &= (x_\lambda - iy_\lambda)(x'_\lambda - iy'_\lambda)(x_\mu - iy_\mu)(x'_\mu - iy'_\mu) \\ &= (\delta_{\lambda\mu} - z_\lambda z_\mu + i\epsilon_{\lambda\mu\nu}z_\nu)(\delta_{\lambda\mu} - z'_\lambda z'_\mu + i\epsilon_{\lambda\mu\nu}z'_\nu) \\ &= (1 - \hat{\mathbf{z}} \cdot \hat{\mathbf{z}}')^2 \end{aligned} \quad (3.7)$$

Substituting into (3.5), we get the main result

$$\delta E = -\frac{S^2}{2} \sum_{i,j} \frac{J_{ij}^2}{h_i + h_j} (1 - \hat{\mathbf{n}}_i \cdot \hat{\mathbf{n}}_j)^2 \quad (3.8)$$

Is there a small parameter in this expansion? The small parameter which justifies keeping just the harmonic-order term is $1/S$, as always in a Holstein-Primakoff expansion, and so the selection term is of order $1/S$ relative to the classical energy. expansion at *harmonic* order. But we made a second, more brutal approximation of the harmonic-order in treating the second term in (3.3) as a perturbation: both terms there are

of order S and of course $h_i \equiv S|\sum_j J_{ij}\hat{\mathbf{n}}_j|$ is manifestly of order J_{ij} . The implicit parameter of this second approximation is evidently “ J/h_0 ” where J is an appropriately weighted average of the couplings, and h_0 is the averaged local field on (if that is not already uniform). Then $h_0 \sim Jz$, where z is an appropriately weighted count of the nearest neighbors. Thus, we are implicitly making *large coordination number* approximation. It should work best on the fcc lattice ($z = 12$), or in lattices with J_2 comparable to J_1 . One expects it to be poorer quantitatively in (say) the nearest-neighbor Kagomé lattice ($z = 4$). However, a biquadratic form with a fitted coefficient might still be a reasonable approximation of the actual functional form in that case.

Expanding the square in (3.8) gives a constant term, a renormalization of the coupling due to fluctuation so (in terms of the unit spins $\{\hat{\mathbf{n}}_i\}$)

$$J_{ij}^{\text{unit}} = J_{ij}S^2 - \frac{S}{4h_0}J_{ij}^2 \quad (3.9)$$

and most importantly a term of the same *biquadratic* form as introduced for thermal and dilution selection, Eq. (1.2) with

$$K_{ij} \rightarrow \frac{SJ_{ij}^2}{4h_0}. \quad (3.10)$$

Because of this form quantum fluctuations must favor collinear states. This conclusion extends to all degenerate vector magnets with site-independent h_0 .

C. Comparison to alternate approaches

As mentioned above, in the case of independent sublattices, one obtains an effective Hamiltonian by perturbation in J_1/J_2 , where J_1 is the inter-sublattice coupling. In the case of the J_1 - J -2 square lattice antiferromagnet, the spin-wave dispersion is easy enough to get analytically, namely³⁵.

$$\hbar\omega(\mathbf{q}) = S \left\{ \left(C(\mathbf{q}) - 2J_1[\cos q_x + \cos q_y] \right) \right. \quad (3.11)$$

$$\left. \times \left(C(\mathbf{q}) - 2J_1 \cos \Phi [\cos q_x - \cos q_y] \right) \right\}^{1/2} \quad (3.12)$$

where $C(\mathbf{q}) \equiv 4J_2(1 - \cos q_x \cos q_y)$. Integrating the zero-point energy over the zone and expanding to second order, we get the spin wave energy (per unit cell)

$$E_{\text{sw}} = E_{\text{sw}}^{(0)} - \frac{J_1^2}{8J_2} G_{-1} \cos^2 \Phi \quad (3.13)$$

where

$$G_{-1} \equiv \int \frac{d^2\mathbf{q}}{(2\pi)^2} \frac{(\cos q_x - \cos q_y)^2}{1 - \cos q_x \cos q_y} \approx 0.727. \quad (3.14)$$

If we match this with (1.2) (with two bonds per unit cell), noting $\cos^2 \Phi = (\hat{\mathbf{n}}_i \cdot \hat{\mathbf{n}}_j)^2$ for nearest neighbors, and remembering the local field is $h_0/S = 4J_2$, we get

$$K_{ij} = \frac{J_1^2}{4h_0/S} G_{-1}. \quad (3.15)$$

Comparing to (3.10), we see the real-space hopping approach overestimated the biquadratic selection energy by $\sim 33\%$, which is not bad in view of the crudeness of the approximation (and considering that the coordination number is not so large for this lattice.)

Two other tricks have been used, instead of the real-space expansion trick, to arrive analytically at an simple effective Hamiltonian of biquadratic form. The first trick is expanding around an infinite-range model³⁶. Comparing to that helps illuminate the derivation in this paper (Sec. III B, above), since either approach is a way of setting up mean-field approximation. That means breaking up the Hamiltonian as $\mathcal{H}_0 + \mathcal{H}'$ such that \mathcal{H}_0 has a trivial (and tractable) state that approximates the ordered state of interest, and expanding in \mathcal{H}' .

Just as in statistical mechanics, there are two standard ways to set up the mean-field theory in real space. In the approach of Sec. III B, \mathcal{H}_0 consisted of local fields that fix each spin in its classical direction, and the wavefunction is a direct product of spin coherent states. On the other hand, in Ref. 36, \mathcal{H}_0 consists of infinite-range spin-spin couplings J_{ij} ; they depend on the sublattice of i and j , but are unchanged if either site is translated by any number of (magnetic cell) lattice vectors. The latter approach, then, is limited to states with a known kind of long-range order, such as face-centered cubic antiferromagnets, and cannot be used for highly frustrated antiferromagnets, which have a huge ensemble of non-periodic classical ground states. (Strictly speaking, the infinite-range approach is not even well posed if this ordered state gets modified into a texture with slowly varying directions, or if it has thermal spinwave fluctuations. Thus, the advantage of the local-fields formulation is that it handles arbitrary configurations of classical directions $\{\hat{n}_i\}$. On the other hand, an advantage of the infinite-range formulation³⁶ is that it explicitly obtains finite-size corrections in the spin-wave selection energies. (The corrections are big at system sizes tractable by exact diagonalization.) In the systems where both approaches apply, they give the same answer³⁶.

A second trick works in the case of a pyrochlore lattice (or any other lattice made of corner sharing triangles and tetrahedra). The sum in (3.4) can be represented as the trace of the square root of the dynamical matrix (basically \mathcal{H}'). A Taylor expansion of that square root gave a series of terms which depend on the classical directions of each spin.^{33,34}

That was only applied to collinear ground states, but (see Sec. V of Ref. 34) it works with small modifications for any ground state configuration. It seems that the second order term of that expansion is identical to the result we found here. (In the collinear case, this term was trivial, and nontrivial effects were found only in higher-order terms representing loops in the lattice.) The trace viewpoint, however, is more powerful in that it allows computation of higher terms; also, in some cases partial resummations of higher terms might give better numerical approximations for the coefficient in the effective Hamiltonian, analogous to the resummations in Ref. 34.

D. Kagomé and similar antiferromagnets

For some frustrated magnets, the effective Hamiltonian (3.8) takes the same value in every classical ground state and hence does not break the degeneracy. In particular, this happens for lattices (such as the kagomé) built from triangles, each of which has a 120° spin arrangement in a ground state. Since $\hat{n}_i \cdot \hat{n}_j = -1/2$ for all nearest neighbor pairs, Eq. (3.8) reduces to a constant.

In such systems, *coplanar* states are the closest thing to collinear states within the ground state manifold, and these indeed have the lowest harmonic zero-point energy.

What would be the natural terms in an effective Hamiltonian, analogous to (3.8) and (1.2)? Since three spins are required to distinguish a coplanar from a noncoplanar state, one might think a term is needed of form

$$|\hat{n}_i \cdot \hat{n}_j \times \hat{n}_k|^2 = 1 - (\hat{n}_i \cdot \hat{n}_j)^2 - (\hat{n}_j \cdot \hat{n}_k)^2 - (\hat{n}_k \cdot \hat{n}_i)^2 + 2(\hat{n}_i \cdot \hat{n}_j)(\hat{n}_j \cdot \hat{n}_k)(\hat{n}_k \cdot \hat{n}_i). \quad (3.16)$$

The simplest spin term which selects for the coplanar states is just a *second-neighbor* biquadratic term of form Eq. (1.2). (In a nearest-neighbor Heisenberg model, that would not get generated by (3.8).) On the kagomé lattice (and other lattices of corner-sharing triangles), the third-neighbor coupling K_3 (for spins in the same row, not across a hexagon) must be equal to the second-neighbor term K_2 , for two reasons:

- (i) if it were not, this would split the degeneracy between different *coplanar* states, whereas we know they are exactly degenerate according to the harmonic-order selection energy
- (ii) at the perturbation order that this term mostly comes from, there is no distinction between paths to these two neighbor-of-neighbor sites.

An extension of the Sec. III B calculation to fourth order perturbation theory does generate the desired neighbor-of-neighbor biquadratic terms on the kagomé lattice. (The trace form from Sec. V of Ref. 34 is probably an easier way to set this up.) Specifically, K_2 and K_3 come from processes involving a string of sites i, j , and k (not on the same triangle). There is a spin exchange involving the pair (ij) , another involving (jk) , and then the same two pairs (in either order) so that we return to the ground state of the trivial Hamiltonian \mathcal{H}_0 ³⁷.

The phenomenological term adopted in Ref. 38 is the same term that would follow from the second-neighbor biquadratic interactions. (This was assumed as the barrier potential to estimate a spin-tunneling amplitude in the kagomé antiferromagnet³⁸.)

Unfortunately, this functional form is wrong for the Kagomé case³⁹, and for coplanar states in general. Instead, the effective Hamiltonian scales non-analytically as $|\sin \theta|$, where θ is the angle between the spin planes in adjoining parts of the lattice³⁴. Sec. V of Ref. 34 has clarified why the spin-wave energy cost, when spins rotate out of one of the discretely selected ground states, scales linear in angle

deviations for the (coplanar) Kagomé case but quadratic for the (collinear) pyrochlore case. This cusp should get somewhat rounded once *anharmonic* fluctuations are taken into account³⁸. It is an interesting, unsolved challenge how to formulate the calculation of a local effective Hamiltonian, in the spirit of (3.8), that captures the cusp behavior.

Nevertheless, a phenomenological form favoring coplanarity, such as a neighbors-of-neighbors biquadratic term, would be an improvement over classical simulations that do not account at all for quantum effects. In static correlations, as can be accessed by Monte Carlo⁴⁰, one expected effect would be a much more robust stabilization of coplanar states (at much higher temperatures). In the dynamics, as can be simulated by molecular dynamics⁴¹, the coplanarity term gives a finite frequency to the band of zero-frequency spin wave modes (except the Goldstone mode).

IV. DISCUSSION

To summarize, we have derived effective Hamiltonian terms for selection free energies from spin wave fluctuations due to thermal excitation, quantum zero-point motion, or to dilution disorder; the result has the form of an effective biquadratic Hamiltonian (1.2) in every case, with the coefficient proportional to temperature, $1/S$, or dilution concentration, respectively. In each of the three cases, our key trick was to rework the problem until the spin configuration became the entries in a matrix, and then expanding in them. The same idea has, in one guise or another, been successful for several independent examples of getting an effective Hamiltonian by integrating out fluctuations. Besides Ref. 2, which is a precursor (for the classical undiluted fcc lattice) of our calculation in Sec.II, this was done for quantum⁴² or classical⁴³ kagomé systems, as well as pyrochlore antiferromagnets^{34,44}.

Sometimes, it is possible to compute numerical energies for a large database of configurations, and then fit an effective Hamiltonian empirically⁴⁴. Even that brute-force approach depends critically on analytics which suggest the proper functional form to be used for fitting.

Now we turn to the applications of effective Hamiltonians. They are convenient for predicting the ground state spin pattern, when the Hamiltonian is complicated by too many kinds of interactions, e.g. spin anisotropies of all sorts, dipolar interactions, distant-neighbor couplings, external fields, or magnetoelastic couplings; also, defects, inhomogeneities, boundaries and domain walls. Thus, they allow quick understanding of phase diagrams which may have many parameters. For example, phenomenological biquadratic term representing the quantum fluctuations was used⁴⁵ to explain a plateau in the dependence on external field of the incommensurate ordering wavevector of CsCuCl_3 . Another one-dimensional model with a biquadratic term was studied in Ref.⁴⁶.

Effective Hamiltonians have also been combined with semiclassical tunneling theory to understand tunneling processes, when degenerate^{36,47,48} or highly degenerate³⁸ ground states are separated by barriers.

A. Pitfalls of classical simulations

As one of us noted in Ref. 15, large S justifies visualizing each spin as a fixed-length vector, but it does *not* justify a purely classical simulation of the system, as is commonly done^{21,40,41,50,51,52,53}. Notwithstanding the well-defined spin directions, the unmodified classical Heisenberg model gives a *qualitatively wrong* picture of the behavior.

The reason can be expressed in terms of different energy scales, as outlined in Ref. 49. The highest scale is $E_J \sim JzS^2$, the scale of the mean-field ordering temperature and Curie-Weiss constant; when $T \ll E_J$ it is already a good approximation that the system is in a classical ground state with small fluctuations. Another scale is the temperature T^* where ordering, freezing, or other phase transitions take place: by definition, a “highly frustrated” magnet¹ is one in which $T^*/T_{\text{MF}} \ll 1$; the ratio can approach 10^{-2} . We are usually interested in lower temperatures $T \sim T^*$, where the interesting changes occur.

The scale which has been ignored is that of harmonic spin-wave fluctuations, $E_{\text{coll}} \sim JS \lesssim E_J$. As long as $E_{\text{coll}} < T < E_J$, the system is certainly classical. But we’re most interested in $T \sim T^* \ll E_{\text{coll}}$, where a classical description is *not* valid. Consider for example¹⁵ the energy barriers against flipping from one collinear (or coplanar) state to another: those due to spin-wave zero-point energy are greater (by the ratio E_{coll}/T) than the classical barriers. That will drastically affect any thermally activated dynamics, and will enhance the ordering tendency (e.g. a large S pyrochlore antiferromagnet will develop a long range order at some $T > 0$). Indeed, in the $T < E_{\text{coll}}$ regime where the classical fluctuations are just a small correction to the quantum fluctuations, the T -dependent selection free energy does not have the form it does in a purely classical model⁵⁴.

I believe there is an easy fix: if the phenomenological term (1.2) (or whatever is appropriate for the system in question) is added to the classical Hamiltonian by hand, the modified classical simulation *can* closely represent the low-temperature behavior. Of course, such a simulation are much tractable (in terms of temperatures, system sizes, and observables) than quantum Monte Carlo. This could be incorporated both into Metropolis Monte Carlo (MC), for modeling the thermodynamics and phase transitions, as well as molecular dynamics, for modeling spin-wave excitations or magnetic relaxation behaviors. (If quantitative results are needed, it would be best to empirically fit the coefficients in (1.2) first.) Occasionally a more exact selection free energy has been used in MC simulations⁵⁵, but that is enormously cumbersome (requires diagonalizing an $O(N)$ dimensional dynamical matrix every MC step.) Having the form of a local effective Hamiltonian makes it very easy to allow for the quantum effects, which is necessary if the simulation means to represent a Heisenberg magnet realistically.

Acknowledgments

This work was supported by NSF grant DMR-DMR-0552461 and its predecessors. We thank Assa Auerbach, Evgenii Shender, Uzi Hizi, Roderich Meissner, and Tom Kaplan for helpful conversations. The original work was completed at Boston University.

APPENDIX A: ALTERNATIVE METHOD OF DILUTION SELECTION

We explore an alternative method of calculating the dilution selection energy E_{dil} , using Lagrange multipliers to enforce the unit length constraints. Rather than the model dilution employed in Sec.II, we consider the more realistic case

$$J_{ij} \rightarrow J_{ij}\epsilon_i\epsilon_j \equiv p^2 J_{ij} + \eta_{ij} J_{ij}, \quad (\text{A1})$$

where $\eta_{ij} \equiv \epsilon_i\epsilon_j - p^2$ for $(i \neq j)$. Here $\epsilon_i = 1$ with probability p and is otherwise zero. Thus $\langle \eta_{ij} \rangle = 0$. Then,

$$\delta H_{\text{dil}} = p^2 \delta H + \delta H', \quad (\text{A2})$$

where $\delta H = \frac{1}{2} \sum_{i,j} A_{ij} \sigma_i \cdot \sigma_j$, and

$$\delta H' = E_0 - \frac{1}{2} N h_0 p (1-p) + \delta H_{\text{REF}} + \delta H_1. \quad (\text{A3})$$

The random exchange field contribution is

$$\delta H_{\text{REF}} = \frac{1}{2} \sum_{ij} A_{ij} \eta_{ij} \mathbf{S}_i^{(0)} \cdot \mathbf{S}_j^{(0)}, \quad (\text{A4})$$

which averages to zero and is ignored as before for computing selection, and

$$\delta H_1 = \sum_i \sigma_i \cdot \mathbf{h}_i. \quad (\text{A5})$$

Here

$$\mathbf{h}_i = \sum_j A_{ij} \eta_{ij} \mathbf{S}_j^{(0)}, \quad (\text{A6})$$

for realistic dilution, or

$$\mathbf{h}_i = \sum_j A_{ij} \epsilon_j \mathbf{S}_j^{(0)}, \quad (\text{A7})$$

for the model dilution of (2.2). To minimize the total zero temperature energy with respect to the spin deviations σ_i for a *fixed* configuration of the quenched disorder variables η_{ij} , we need to include a Lagrange multiplier λ_i to ensure that the unit length constraints $\sigma_i \cdot \mathbf{S}_i^{(0)} = 0$ are obeyed, yielding

$$p^2 \sigma_i = -(A^{-1})_{ij} (\mathbf{h}_j + \lambda_j \mathbf{S}_j^{(0)}). \quad (\text{A8})$$

Introducing a matrix notation as in Sec.II the λ_i are determined by the constraint equation to be

$$\lambda = -\mathbf{B}^{-1} \mathbf{P} \mathbf{A}^{-1} \mathbf{h}. \quad (\text{A9})$$

When (A9) is substituted into (A8), and the result substituted into (A2), we obtain an expression for the total energy in the presence of the specific configuration of dilution variables:

$$p^2 \delta H + \delta H_1 \equiv E_{\text{dil}} = \frac{1}{2} p^{-2} (\mathbf{h}^T \mathbf{A}^{-1} \mathbf{P}^T \mathbf{B}^{-1} \mathbf{P} \mathbf{A}^{-1} \mathbf{h} - \mathbf{h}^T \mathbf{A}^{-1} \mathbf{h}) \quad (\text{A10})$$

identical to (2.17).

Both terms take the form $\mathbf{h}^T \mathbf{M} \mathbf{h}$, which must now be averaged over the disorder. In components the average becomes

$$\sum_{\mu\nu} \sum_{ijkl} M_{i\mu,j\nu} S_{l\mu}^{(0)} S_{k\nu}^{(0)} A_{il} A_{jk} \langle \eta_{il} \eta_{jk} \rangle. \quad (\text{A11})$$

The average is

$$\begin{aligned} \langle \eta_{il} \eta_{jk} \rangle &= p^3 (1-p) (\delta_{ij} + \delta_{ik} + \delta_{lj} + \delta_{lk}) \\ &+ p^2 (1-p)^2 (\delta_{ij} \delta_{lk} + \delta_{ik} \delta_{lj}), \end{aligned} \quad (\text{A12})$$

if we also replace the \mathbf{A} 's in (A11) by \mathbf{J} 's to ensure that $i \neq l, j \neq k$. The terms proportional to $(1-p)$ represent effects of independent missing spins (defects), and will be seen to reproduce the form of E_{dil} calculated in Sec.II. The $(1-p)^2$ terms account for pairwise correlations between different defects. Thus,

$$\begin{aligned} \langle \mathbf{h}^T \mathbf{M} \mathbf{h} \rangle &= p^3 (1-p) \text{Tr} [h_0 \mathbf{P} \mathbf{J} \mathbf{M} \mathbf{P}^T + h_0 \mathbf{P} \mathbf{M} \mathbf{J} \mathbf{P}^T + \\ &\quad \mathbf{P} \mathbf{J} \mathbf{M} \mathbf{J} \mathbf{P}^T + h_0^2 \mathbf{P} \mathbf{M} \mathbf{P}^T] + p^2 (1-p)^2 \times \\ &\times \sum_{ij,\mu\nu} J_{ij} J_{ij} S_{i\nu}^{(0)} [S_{j\mu}^{(0)} M_{j\nu,i\mu} + S_{i\mu}^{(0)} M_{j\nu,j\mu}] \end{aligned} \quad (\text{A13})$$

It is now straightforward to evaluate E_{dil} by substituting (A13) in (A10). Note that the second term in (A13) is smaller than the first by order $1/z$ where z is the coordination number ($z = 12$ or 18 for face-centered cubic, depending whether J_2 is included.) After performing simplifications we find the dilution energy

$$\begin{aligned} E_{\text{dil}} &= \frac{1}{2} p (1-p) [\text{Tr} \mathbf{B}^{-1} - N h_0] \\ &+ \frac{1}{2} (1-p)^2 \left[+ \frac{1}{2} (1-p)^2 \left[\sum_{ij,\mu\nu} J_{ij} J_{ij} S_{i\nu}^{(0)} \times \right. \right. \\ &\quad \left. \left(S_{j\mu}^{(0)} [\mathbf{A}^{-1} \mathbf{P}^T \mathbf{B}^{-1} \mathbf{P} \mathbf{A}^{-1} - \mathbf{A}^{-1}]_{j\nu,i\mu} \right. \right. \quad (\text{A14}) \\ &\quad \left. \left. + S_{i\mu}^{(0)} [\mathbf{A}^{-1} \mathbf{P}^T \mathbf{B}^{-1} \mathbf{P} \mathbf{A}^{-1} - \mathbf{A}^{-1}]_{j\nu,j\mu} \right) \right] \end{aligned} \quad (\text{A15})$$

(Some simplifications of the $\mathcal{O}(1-p)^2$ terms are possible, but the result cannot be written in terms of conventional matrix operations.)

Clearly the first term in (A15) is just the dilution part of (2.21) of Sec.II if $\langle \epsilon^2 \rangle$ is identified with $(1-p)/p$ (after rescaling $J_{ij} \rightarrow J'_{ij} = J_{ij} p^2$). As argued in Sec.II $E_{\text{dil}} = 0$ for any collinear state. Here this is clearest from examination of (A8). In a collinear state ($T = 0$), all the $\mathbf{S}_i^{(0)}$ may be taken along the $\hat{\mathbf{z}}$ axis. Then clearly the only allowed directions for σ_i

fluctuations are in the xy -plane, eliminating the second two terms from (A8) and forcing $\sigma_i = 0$ for all i . Clearly then $E_{\text{dil}} = 0$. On the other hand the form of $p^2\delta H + \delta H_1$ shows that in a generic noncollinear case, where $\sigma_i \neq 0$, the dilution energy for *every* realization of the quenched fluctuations will be reduced—the system takes advantage of the fluctuation. Thus for a generic noncollinear state, we must have $E_{\text{dil}} < 0$ strictly.

Systems with an *exceptional* degeneracy may have $E_{\text{dil}} = 0$ even for noncollinear states. For example, the 2D XY square lattice AF with $J_2 < 0$ and $J_1 = 0$. Then the system forms two *decoupled* simple antiferromagnetic sublattices. The coupling from the dilution then comes only from spins on the same sublattice, which are collinear. Thus $E_{\text{dil}} = 0$ even though the total spin configuration is noncollinear.

It should be emphasized that the terms above are not the only contributions of $\mathcal{O}(1-p)^2$, since neglected terms of order σ_i^3 also contribute. Only in a case where some small parameter controls the size of the σ_i will the exhibited terms give the dominant $\mathcal{O}(1-p)^2$ contribution.

APPENDIX B: EFFECTS OF MAGNETOELASTIC COUPLING

It is well-known that exchange striction, an *isotropic* effect of nonzero magneto-elastic coupling, also leads to an effective biquadratic exchange. It is long known these favor collinear states, e.g. in MnO, and they play important roles in highly frustated spinels⁵⁶. To see how the biquadratic form arises in this case, we add to the Hamiltonian the elastic energy H_{el} and magneto-elastic coupling H_{me} . The elastic energy is

$$H_{\text{el}} = \frac{1}{2} \int d^3x \varepsilon_{\kappa\lambda} \varepsilon_{\mu\nu} . \quad (\text{B1})$$

Here $\varepsilon_{\kappa\lambda}$ is the strain tensor, and $\{c_{\kappa\lambda\mu\nu}\}$ are the elastic constants, separately symmetric in $(\kappa\lambda)$ and $(\mu\nu)$, and under their interchange. (We use the summation convention for component indices.) The magneto-elastic coupling is given by

$$H_{\text{me}} = \frac{1}{2} \sum_{ij} \varepsilon_{\kappa\lambda} \kappa_{ij} \alpha_{ij}^{\kappa\lambda} \mathbf{S}_i \cdot \mathbf{S}_j , \quad (\text{B2})$$

obtained simply by expanding the exchange constants in lattice displacements. Thus the magneto-elastic constants are defined by

$$\alpha_{ij}^{\kappa\lambda} = -(\mathbf{r}_{ij})_{\kappa} \frac{\partial J_{ij}}{\partial (\mathbf{r}_{ij})_{\lambda}} \quad (\text{B3})$$

Next the energy $H_{\text{el}} + H_{\text{me}}$ is minimized with respect to the strains ε_{kl} and the result substituted back in this expression. The result is

$$H_{\text{me}}^{\text{eff}} = -\frac{1}{8} \sum_{ij} \sum_{kl} [c^{-1}]_{\kappa\lambda\mu\nu} \alpha_{ij}^{\kappa\lambda} \alpha_{kl}^{\mu\nu} (\mathbf{S}_i \cdot \mathbf{S}_j) (\mathbf{S}_k \cdot \mathbf{S}_l) . \quad (\text{B4})$$

This has the biquadratic form. Within the ground state manifold (B4) has an expression in terms of the same quartic invariants mentioned at the end of Sec. II B.

To estimate the size of this effect, we assume the exchange constants decay rapidly with distance, according to $J(r) = J_0(r/r_0)^{-f}$,⁵⁷ yielding

$$\alpha^{\kappa\lambda}(\mathbf{r}) \approx -\frac{f}{2} \frac{r_{\kappa} r_{\lambda}}{r^2} J(r) . \quad (\text{B5})$$

There is some evidence that for superexchange, f is between 10,⁵⁸ and 14.⁵⁷

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